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CASE SCHOOL OF APPLIED SCIENCE.

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PETROLEUM.*

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INVESTIGATIONS ON THE COMPOSITION OF
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BY CHARLES F. MABERY.

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No. 35.—ON THE COMPOSITION OF CALIFORNIA
PETROLEUM.

BY CHARLES F. MABERY AND EDWARD J. HUDSON.

IN its composition as a natural product, California petroleum is the most interesting of any of the numerous petroleums that have come under our observation. When its constituents are more fully understood they will doubtless shed new light on the origin of petroleum, from the fact that they have been subjected to less rigorous agencies during, or subsequent to, their formation than petroleums from other well-known fields. In fields not yet developed, such as those of South America and Japan, similar unstable oils are found. It is useless to attempt to separate from these peculiar oils their individual constituents by the ordinary method of fractional distillation under atmospheric pressure. Not only on account of the high boiling points, but because the presence of air causes such decomposition, hydrocarbons boiling above 200° cannot be separated in a pure form without the aid of a vacuum. With no further knowledge of the constituents of the crude oils, this explains the numerous ineffectual attempts during the last thirty years to obtain acceptable refined products from California petroleum. By excluding air, as in vacuum distillation, with the reduction of boiling points, it is possible to distil without decomposition all the hydrocarbons of the crude oils. With some modifications of the apparatus employed in vacuum distillation of the higher fractions of Pennsylvania oil, the fractional separation may be carried on with little more delay than in distillation under atmospheric pressure.

Provision for drawing in fresh fractions without loss of vacuum may be made by sealing on a second tube to the neck of the flask a little lower than the exit tube for the escaping vapors. Then, as in the ordinary application of the Hempel principle, the cooling space in the neck of the flask may be increased by filling it with broken glass. This requires a long-necked flask, and the beads may be supported on a piece of glass rod resting on the bottom of the flask, the upper end flattened so as nearly to fill the neck of the flask as a support to the broken glass. The chief hindrance to the use of beads is the condensation of liquids with high boiling points in the neck of the flask, due to the cooling effect of the outside air. The neck of the flask must, therefore, be packed an inch or more thick with asbestos. With this arrangement, and with a flat perforated ring burner for heating, the distillation may be conducted with a fairly rapid fractional separation, without decomposition even of the constituents that distil above 350°, 50 mm.

This examination of California oil was undertaken with the intention of ascertaining the series of hydrocarbons which constitute the main body of the crude oil, as well as the principal members of the series, as shown by percentage composition and molecular weights.

The first specimen of crude oil was received through the kindness of Mr. C. A. Black, chemist in an oil company in Ventura County. The second specimen came from a well of the Coalinga Oil Company in Fresno, through the secretary of the company, Mr. Henderson Hayward. These two specimens will be referred to respectively as Ventura oil and Fresno oil. Another specimen was received from the Puente Hills in Los Angeles County, through the kindness of the Puente Oil Company at Chino. This oil will be referred to as Puente oil. Four other specimens were received from the Torrey wells and the "Los Angeles" wells in the Sespe district (Scott's Hill) in Ventura County, through the kindness of the Union Oil Company at Santa Paula. These samples will be designated respectively as Adams' Cañon, Bardsdale, Scott's Hill, and Torrey oils.

Another specimen is of especial interest, since it came from a well sunk beneath the Pacific Ocean at high tide. It was sent by Mr. J. B. Treadwell from a well at Summerland, Santa Barbara County, at a point where the oil strata outcropped on a north and south line at the top of an elevation, and again descending on the south side, disappeared under the ocean. The well was driven to a depth of 245 feet, just within the shore line at high tide, where it reached the bottom of the oil sand. This oil will be referred to as Santa Barbara oil.

This collection of specimens seemed to offer a fair average of the oils from the California fields, representing four different counties, and deposits that yield oil in considerable quantities.

Since these crude oils differed essentially in their appearance and in their physical properties, in ascertaining their composition it seemed advisable to examine them individually.

In the spring of 1897 an examination of the Ventura oil was begun,* and besides giving the composition of the crude oil, the fractional separations were carried far enough *in vacuo* to identify the principal constituents boiling below 175°. The several hydrocarbons homologous with benzol, which have been found in petroleum from other sources, were found to constitute a large part of the unpurified distillates; but the chief constituents were shown by their composition and specific gravity to be methylenes, for the first time recognized as essential constituents of American petroleum.

PETROLEUM FROM FRESNO COUNTY.

A brief account of the composition of a specimen of crude oil from Fresno County was given in the preliminary paper referred to above. When this oil was subjected to distillation, it was evident that decomposition could only be prevented in the fractions above 150° by collecting them *in vacuo*. The portion collected below 150° atmospheric pressure — 2090 grms. — was submitted to long continued fractional separation within 1° until 50 grms. collected below 55°, and only 5 grms. between 55° and 68°. At 68°—70° the distillates amounted to 60 grms., which was separated for the most part at 68°. The specific gravity of the crude distillate at 68° was found to be 0.6913, and after thorough agitation with fuming sulphuric acid, 0.6844. A combustion of the purified oil gave the following percentages of carbon and hydrogen: —

0.1692 grm. of the oil gave 0.5234 grm. CO₂ and 0.2314 grm. H₂O.

		Calculated for		Found.
	C ₈ H ₁₆ .	C ₈ H ₁₈ .		
C	85.70	83.72		84.38
H	14.30	16.28		15.30

The loss in this analysis is doubtless due to an escape of a very small amount of gaseous decomposition products without complete combustion. Combustion of such a volatile oil requires the closest attention in manip-

* Am. Chem. Journ., XIX. 796 (1897).

ulation to avoid loss in transferring to the combustion tube, and as will appear later, the highest temperature that the hardest tube will stand is necessary for complete combustion. These results seem to indicate that the oil was a mixture of hexane and hexamethylene. The slight change in specific gravity after treatment with fuming sulphuric acid and potassic hydrate shows that the benzol had been almost completely removed. The fractions at 68° appear to be the last in California oil containing members of the series C_nH_{2n+2} . Since small quantities of distillates collected in the vicinity of 60°, 38°, and in one specimen at 30°, it is probable that the very light gasoline from California oil has the same composition as that from Pennsylvania oil.

The specific gravity of hexane, 0.6630 at 18°, and of hexamethylene, 0.690, also indicate that the fraction 68°-70° is a mixture of these two hydrocarbons.

HEPTAMETHYLENE, C_7H_{14} .

The distillate collected at 96°-98° amounted to fifty grams. Before purification it gave as its specific gravity 0.7499, and after purification, 0.7413. The specific gravity of heptane boiling at this point is 0.6440 (20°.5). Beilstein and Kurbatoff gave 0.742 at 18° as the specific gravity of heptanaphthene. A combustion gave the following percentages of carbon and hydrogen:—

0.1413 grm. of the purified oil gave 0.4442 grm. CO_2 and 0.1814 grm. H_2O .

	Calculated for C_nH_{2n} .	Found.
C	85.70	85.74
H	14.30	14.35

A determination of the vapor density of the fraction 96°-98° by collecting the vapor over mercury gave a value corresponding to the molecular weight of heptamethylene. The determination was made by the method of V. Meyer, *in vacuo*, essentially according to the modification of Lunge and Neuberg: *—

0.0494 grm. of the oil gave 22.9 c.c. under a tension of 373 mm. and at 24°.

Calculated for C_7H_{14} .	Found.
3.40	3.40

* Ber. deutsch. Gesell., 1891, 729.

The high specific gravity of this hydrocarbon corresponding to that of heptanaphtene, the composition given by analysis and the molecular weight, leave no doubt that this body is a heptamethylene, and that heptane is not contained in California (Fresno County) petroleum.

BENZOL.

The distillates in the vicinity of 80°, especially 79°–81°, gave the characteristic odor of benzol. 20.5 grms. of these fractions shaken below 60° with a mixture of nitric and sulphuric acids, gave a heavy nitro-product; after washing with water and distilling, the distillate weighed 13 grms., showing that 35.5 per cent of this oil was benzol. Some of the same fractions treated with fuming nitric acid deposited needle-shaped crystals that melted at 89°–90°, the melting point of dinitrobenzol.

TOLUOL.

After the twelfth distillation, 60 grms. collected at 109°–110° with the penetrating odor of toluol. 30 grms. of this distillate was shaken with a mixture of nitric and sulphuric acids, and the oil not nitrated separated from the nitro-product by distillation. The distillate weighed 13 grms., showing that 54 per cent of the original distillate was toluol. Upon agitating this product with fuming sulphuric acid and distilling, 1.6 per cent more was removed. The remaining oil was dried over sodium for analysis.

The unpurified distillate gave the following values on analysis: —

0.1584 grm. of the oil gave 0.5090 grm. CO₂ and 0.1663 grm. H₂O.

	Calculated for	Found.
	Toluol.	C _n H _{2n} .
C	91.31	85.70
H	8.69	14.30

The change in composition by treatment with acids was very marked: —

0.1725 grm. of the purified oil gave 0.5387 grm. CO₂ and 0.2282 grm. H₂O.

	Calculated for C _n H _{2n} .	Found.
C	85.70	85.20
H	14.30	14.71

Evidently the small quantity of oil remaining after the treatment with acids was octonaphtene, that had not been completely separated by distillation.

OCTONAPHTENE, C_8H_{16} .

After the twentieth distillation, 30 grms. collected at 118° – 120° , which, with no further purification than drying over sodium, gave 0.7615 as its specific gravity at 20° , and, on analysis, values required for octonaphcene:—

0.1457 grm. of the oil gave 0.4566 grm. CO_2 and 0.1922 grm. H_2O .

C	85.47
H	14.71

After thorough treatment with fuming sulphuric acid the specific gravity was reduced to 0.7532, at 20° (octonaphcene, 0.7582 at $17^\circ.5$, Beilstein and Kurbatoff), but the composition was scarcely changed:—

I. 0.1471 grm. of the oil gave 0.4618 grm. CO_2 and 0.1895 grm. H_2O .
 II. 0.1334 grm. of the oil gave 0.4185 grm. CO_2 and 0.1762 grm. H_2O .

	Calculated for C_nH_{2n} .	Found.	
		I.	II.
C	85.70	85.62	85.54
H	14.30	14.32	14.67

After the eighteenth distillation, 25 grms. remained persistently at 124° – 125° , which was not affected by fuming sulphuric acid in the cold, but at 100° the acid became colored and gave off much SO_2 . On pouring into water, the solution gave a peculiar odor resembling turpentine, and a black powder separated that contained nitrogen. Analysis of the distillate after the treatment with the acid gave values required for C_nH_{2n} :—

0.1391 grm. of the oil gave 0.4354 grm. CO_2 and 0.1875 grm. H_2O .

	Required for C_nH_{2n} .	Found.
C	85.70	85.36
H	14.30	14.98

Since no other hydrocarbon than normal octane has been recognized with this boiling point, this distillate must be a mixture of octonaphcene with a higher body, but evidently normal octane is not present in appreciable quantity.

NONONAPHTENE, C_9H_{18} .

A considerable quantity of distillate collected at 134° – 135° , that gave as its specific gravity 0.8175. After purification with fuming sulphuric

acid its specific gravity was reduced 0.7591. 28 grms. of the crude distillate gave 13 grms. of the purified oil with a loss of 53 per cent. The purified oil gave by the action of fuming nitric acid a nitro-derivative that, after crystallization from glacial acetic acid, melted at 85°. The melting point of dinitromesitylene is 86°. A combustion of the purified distillate gave values for carbon and hydrogen required for nononaphtene:—

0.1382 grm. of the oil gave 0.4318 grm. CO_2 and 0.1827 grm. H_2O .

	Calculated for C_9H_{18} .	Found.
C	85.70	85.21
H	14.30	14.68

XYLOLS.

Since para- and meta- xylols have frequently been found in petroleum, it did not seem advisable to separate the isomeric xylols, although the distillates 137°–140° gave the strong penetrating odor of these bodies. At the end of the thirteenth distillation, 630 grms. collected within these limits. On treating 125 grms. of this product with a mixture of nitric and sulphuric acids, and agitating below 60°, washing with sodic hydrate and water, drying and distilling, only 50 grms. came over below 145°, showing that the xylols formed 60 per cent of the original distillates and had been removed as nitro-products. At the low temperature of the nitration only the aromatic hydrocarbons could have been affected. The change in composition by the nitration is shown by the following analyses:—

0.1469 grm. of the unpurified oil gave 0.4770 grm. CO_2 and 0.1495 grm. H_2O .

	Calculated for Xylol.	Found.
C	92.31	88.53
H	7.69	11.31

Analysis of the purified distillate gave the following results on analysis:—

- I. 0.1382 grm. of the oil gave 0.4318 grm. CO_2 and 0.1827 grm. H_2O .
- II. 0.1386 grm. of the oil gave 0.4318 grm. CO_2 and 0.1837 grm. H_2O .
- III. 0.1441 grm. of the oil gave 0.4492 grm. CO_2 and 0.1901 grm. H_2O .

	I.	II.	III.	C_nH_{2n} .
C	85.21	84.96	85.00	85.70
H	14.69	14.72	14.66	14.30

The chief portion of the nitrated oil was shown to be meta xylol, since the nitro-compound distilled at 240° - 260° , and with fuming nitric acid it was converted into a crystalline powder insoluble in alcohol; crystallized from glacial acetic acid, it melted at 176° , the melting point of trinitrometaxylol. Probably the fifty grams not nitrated was for the most part nononaphtene.

NONANE.

Since considerable quantities of distillates collected in the vicinity of 150° , after the seventeenth distillation, attempts were made to ascertain whether nonane is a constituent of California petroleum. This seemed of especial importance since nonane forms such an important constituent of Pennsylvania petroleum. Without purification a combustion showed the following proportions of carbon and hydrogen: carbon, 86.14; hydrogen, 12.67. The specific gravity was 0.8117. After agitating several times with fuming sulphuric acid, the composition was materially changed:—

0.1719 of the oil gave 0.5372 grm. CO_2 and 0.2206 grm. H_2O .

	Calculated for C_nH_{2n} .	Found.
C	85.70	85.20
H	14.30	14.26

The principal constituent of this fraction was therefore a naphtene or a mixture of napthenes.

DEKANAPHTENE, $C_{10}H_{20}$.

At the end of the seventeenth distillation, the quantity of distillates within one degree limits between 159° and 163° amounted to 150 grms. By further distillation these came together for the most part at 160° - 161° . The specific gravity of the unpurified distillate at 20° was 0.8272. When agitated in the cold with fuming sulphuric acid, this distillate developed great heat; after treatment several times, until the acid was no longer much colored, the product was washed with sodic hydrate and water and dried for analysis. The original distillate lost 75 per cent of its weight by this treatment. The aromatic hydrocarbon

doubtless consisted, for the most part at least, of ethyl toluol, boiling point 161°–162°, but no further attempts were made to identify it.

The specific gravity of the residual oil was 0.7841, practically the same as the specific gravity of dekanaphtene, 0.783, separated by Markownikoff and Oglobine from Baku petroleum. Its odor is precisely similar to that of the corresponding hydrocarbon which one of us (Mabery) has separated from crude Baku oil.

Analysis of the unpurified distillate gave the following values:—

I. 0.1462 grm. of the oil gave 0.4724 grm. CO₂ and 0.1524 grm. H₂O.
 II. 0.1496 grm. of the oil gave 0.4844 grm. CO₂ and 0.1564 grm. H₂O.

		Found.
C	88.10	88.28
H	11.57	11.61

After treatment with the acid the composition was materially changed; the results correspond closely to the composition of dekanaphtene:—

0.1481 grm. of the oil gave 0.4646 grm. CO₂ and 0.1932 grm. H₂O.

	Calculated for C ₁₀ H ₂₀ .	Found.
C	85.70	85.55
H	14.30	14.50

A determination of the molecular weight gave a value required for dekanaphtene.

0.8850 grm. of the oil and 24.22 grms. benzol gave, by the Beckman method, at the freezing point, a depression of 1°.28.

	Calculated for C ₁₀ H ₂₀ .	Found.
	140	140

After the twenty-fourth distillation, 50 grms. collected at 169°–170°, which gave as its specific gravity without purification, 0.8358. After thorough agitation with fuming sulphuric acid and washing, the specific gravity was reduced to 0.7749, but the larger portion of the oil was removed by the acid, indicating that the fraction consisted for the most of a benzol homologue. The small quantity remaining after the treatment was doubtless dekanaphtene, since its specific gravity was nearly the same.

The presence of a naphtene in Russian oil, boiling at 182°, led us to believe that the same body should be found in California oil. But

the small quantity of distillate collecting here, only 10 grms. after long distillation, excluded this hydrocarbon in any appreciable quantity.

UNDEKANAPHTENE, $C_{11}H_{22}$, 195°.

Between 188° and 191°, 50 grms. came together at the end of the tenth distillation, which gave the following results on analysis:—

0.1423 grm. of the oil gave 0.4550 grm. CO_2 and 0.1617 grm. H_2O .

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	87.20
H	14.30	12.63

The specific gravity of this distillate before treatment was 0.8386. After vigorous agitation with fuming sulphuric acid, and washing, the specific gravity was reduced to 0.8044.

A distillate separated from Russian oil at 197° gave (Markownikoff and Oglobline) as its specific gravity at 14°, 0.8055, and it was assigned the formula $C_{12}H_{24}$. The quantity of oil remaining after separation of durol, which no doubt was the benzol hydrocarbon in this distillate, was small. That it was a naphtene, as shown by its specific gravity, is confirmed by analysis:—

0.1459 grm. of the oil gave 0.4575 grm. CO_2 and 0.1886 grm. H_2O .

	Calculated for $C_{12}H_{24}$.	Found.
C	85.70	85.70
H	14.30	14.40

Determinations of the molecular weight of this fraction by the Beckman freezing point method using benzol gave the following value:—

0.7901 grm. of the oil and 24.68 grms. benzol gave a depression of 1.°012.

1.1249 grm. of the oil and 25.90 grms. benzol gave a depression of 1°.36.

Calculated for $C_{11}H_{22}$.	I.	Found.
154	155	157

It appears from these results that the hydrocarbon in California petroleum boiling at 195° is not dodekanaphtene, $C_{12}H_{24}$, but undekanaphtene, $C_{11}H_{22}$. This conclusion is further confirmed, as will appear later, by the composition of the distillate 216°, which appears to be dodekanaphtene,

and still further by the composition of the monochlornaphtene obtained from the hydrocarbon boiling at 195°, which gives as its formula $C_{11}H_{21}Cl$.

In the vicinity of 200°, 50 grms. of a distillate collected which gave as its specific gravity 0.8684. After agitation with fuming sulphuric acid, the specific gravity was diminished to 0.8202. An analysis before treatment gave 87.84 per cent of carbon and 11.91 per cent of hydrogen. After treatment with the acid, the analysis gave 85.99 per cent of carbon and 13.97 per cent of hydrogen, showing that some of the aromatic hydrocarbon still remained; the small amount of naphtene was doubtless undekanaphtene, boiling at 195°; specific gravity, 0.8010, as given above.

DODEKANAPHTENE, $C_{12}H_{24}$.

A considerable quantity of distillate collected at 208°–210°, corresponding to 216°, which corresponded in composition by analysis and molecular weight to dodekanaphtene: —

0.1496 grm. of the oil gave 0.4677 grm. CO_2 and 0.1962 grm. H_2O .

	Calculated for C_nH_{2n} .	Found.
C	85.70	85.26
H	14.30	14.57

Determinations of the molecular weight of this product by the Beckman method at the freezing point, gave results corresponding to the formula of dodekanaphtene.

1.0141 grm. of the oil and 25.61 grms. benzol gave a depression of 1.17.

Calculated for $C_{12}H_{24}$.	Found.
166	166

It is therefore evident that California petroleum differs from Russian oil in containing dodekanaphtene, boiling at 216°, as well as undecanaphtene, boiling at 195°.

PUENTE OIL.

The specimen received from the Puente Oil Company was somewhat thicker than the Fresno oil. Its specific gravity at 20° was found to be 0.892. It contained 0.80 per cent of sulphur. Two determinations of nitrogen by the Kjeldahl method gave, (I.) 0.564, (II.) 0.587; and by the absolute method, measuring the volume of nitrogen, (I.) 1.18, and

(II.) 1.22. A combustion of the crude oil gave, 84.96 per cent of carbon and 11.96 per cent of hydrogen. Two determinations of bromine absorption gave, (I.) 18.8, (II.) 18.3 per cent.

A distillation of 1346 grms. of the crude oil under atmospheric pressure gave the following weights: —

-100°	100° - 150°	150° - 200°	200° - 250°	Grms.
167	170	132	130	

The small proportions distilling below 250° made it evident that the chief constituents could only be separated *in vacuo*. The specific gravity of these distillates at 20° were ascertained by weighing on a Westphal balance: —

100°	100° - 150°	150° - 206°
0.7642	0.8155	0.8538

Ten litres of the Puente crude oil, after collecting below 150° at atmospheric pressure, gave the following weights under 50 mm: —

150 At. Pr.	-120°	120° - 150°	150° - 175°	175° - 185°	185° - 200°	Grms.
590	800	827	990	160	495	

The residue above 200° was next divided into fractions of convenient size without noting temperatures: —

1.	2.	3.	4.	Grms.
655	1010	670	430	

Further distillation of the fraction -150 At. Pressure gave the following weights: —

-60°	60° - 62°	66° - 68°	78° - 82°	88° - 90°	96° - 98°	109° - 110°	118° - 120°	Grms.
10	10	10	27	40	120	60	65	

Smaller weights collected at intermediate temperatures.

HEPTAMETHYLENE, C_7H_{14} .

No attempts were made to ascertain the composition of the individual fractions below 96° from Puente oil. Those portions will receive further attention with the corresponding distillates from the other oils. Without purification the distillate 96° - 98° gave as its specific gravity at 20° , 0.7499. After repeated agitation with fuming sulphuric acid and potassic hydrate, the specific gravity was scarcely changed, 0.7440;

specific gravity of heptanaphtene, 0.742 at 18°. Analysis I. was made of the untreated oil, analysis II. of the portion after treatment:—

I. 0.1409 grm. of the oil gave 0.4438 grm. CO₂ and 0.1683 grm. H₂O.
 II. 0.1396 grm. of the oil gave 0.4383 grm. CO₂ and 0.1792 grm. H₂O.

	Calculated for C ₇ H ₁₄ .	I.	Found.
C	85.70	85.90	85.60
H	14.30	13.27	14.26

The difference in analysis I. is doubtless due to oxygen and nitrogen compounds, since agitation of the crude distillates with potassic hydrate separates from most of the distillates from California petroleum heavy oils, with an odor resembling that of creosote. A description of these oxygenated compounds is reserved for a later paper. The specific gravity of the purified fraction, 0.7440, is essentially the same as that of heptanaphtene separated from Russian oil, 0.748, by Beilstein and Kurbatoff.

OCTONAPHTENE, C₈H₁₆.

The fraction 118°–120°, without further treatment, gave as its specific gravity at 20°, 0.7615, which was reduced to 0.7540 by agitation with fuming sulphuric acid. Specific gravity of octonaphtene, 0.7552 at 17°.5. Analysis I. was made of the crude distillate, and analysis II. of the oil after purification with the acid.

I. 0.1406 grm. of the oil gave 0.4424 CO₂ and 0.1760 grm. H₂O.
 II. 0.1503 grm. of the oil gave 0.4692 grm. CO₂ and 0.1941 grm. H₂O.

	Calculated for C ₈ H ₁₆ .	I.	Found.
C	85.70	85.81	85.20
H	14.30	13.91	14.35

No further examination was made of the fractions from 120° to 148°, but it seemed of interest to ascertain whether nonane formed any part of the distillate 148°–150°, since it forms such a large proportion of the Eastern oils. The crude distillate 150°–151° gave as its specific gravity 0.7910, and after purification with sulphuric acid, 0.7730. Analysis of the treated oil gave percentages of carbon and hydrogen that still showed the presence of the benzol homologue.

0.1449 grm. of the oil gave 0.4589 grm. CO₂ and 0.1807 grm. H₂O.

	Calculated for C _n H _{2n} .	Found.
C	85.70	86.37
H	14.30	13.57

From the results of this analysis it is evident that nonane forms no appreciable proportion of Puente oil.

DEKANAPHTENE, C₁₀H₂₀.

50 grms. of a distillate collected at 160°–162°, with smaller quantities on either side. A determination of its specific gravity at 20° gave 0.7966, and after agitation with sulphuric acid, 0.7745. The composition of this distillate after treatment with the acid was shown by analysis:—

0.1747 grm. of the oil gave 0.5515 grm. CO₂ and 0.2185 grm. H₂O.

	Calculated for C ₁₀ H ₂₀ .	Found.
C	85.70	86.09
H	14.30	13.90

FRACTION 168°–172°.

In all the California oils examined, as stated above, considerable quantities have collected at 168°–172°. Since large proportions of the benzol hydrocarbons appear in all these oils, the distillate 168°–172° might consist to a large extent of pseudocumol, boiling point 168°. The high specific gravity of the fraction before treatment with the acid, 0.8063, and the lower value after treatment, 0.7874, indicates a considerable proportion of the benzol homologue. Even after the acid treatment, the percentages of carbon and hydrogen showed the presence still of the same constituent: carbon, 85.91; hydrogen, 13.61. It seems probable, therefore, that the benzol homologue constitutes the greater part of this distillate, and the residue after treatment is doubtless higher or lower constituents. But the absence of a decane corresponding to the decane in Pennsylvania petroleum, boiling at 172°, is assured.

FRACTION 180°–182°.

Only 10 grms. collected at 180°–182°, with smaller quantities on either side. Although this quantity of the oil was insufficient for complete examination, its specific gravity before and after analysis was ascertained, and an analysis made after treatment with acid. Before treatment the

value obtained was 0.8116, and afterward 0.7955. A combustion gave 86.27 per cent of carbon, and 13.79 per cent of hydrogen. Evidently, like the Fresno oil, Puente oil has no constituent with this boiling point, except perhaps a benzol homologue.

UNDEKANAPHTENE, $C_{11}H_{22}$, 195°.

A naphtene should be expected between 190° and 200°, since undekanaphtene, $C_{11}H_{22}$, is a constituent of the Fresno oil. The 20 grams collecting at 190°–192° gave as its specific gravity at 20°, 0.8196, and after treatment with fuming acid, 0.8046 (0.8055 at 14°, Markownikoff). A combustion of the oil after treatment gave 85.90 per cent of carbon and 13.85 per cent of hydrogen.

The series C_nH_{2n+2} forms no part of the Puente oil, at least above 95°. The low percentage of hydrogen seems to indicate a series still poorer in hydrogen than the naphtenes, especially in the higher distillates, possibly a series C_nH_{2n-2} , containing two naphtene rings. Whether such hydrocarbons are really present, or whether benzol homologues have not been completely removed, will appear in more prolonged distillation of these oils boiling above 200°.

BARDSDALE OIL.

The specimen marked Owens No. 2, sent by the Union Oil Co. from the Bardsdale district, was quite thick and heavy. Its specific gravity at 20° was 0.8923. It contained 1.25 per cent of nitrogen, as shown by the volume of nitrogen collected. A Kjeldahl determination gave 0.50 per cent. A Carius determination gave 1.5 per cent of sulphur, showing it to be a high sulphur oil. A combustion gave 84.17 per cent of carbon and 12.15 per cent of hydrogen. 108 grms. of the oil distilled under atmospheric pressure gave the following weights:—

-150°	150° – 310°	310° – 410°	
9	24	7	Grms.
0.7433	0.8170		Specific gravity.

In distilling 5088 grms. under 50 mm., except -150° the following weights were obtained:—

-150° At. Pr.	150° – 200°	200° – 250°	250° – 290°
250	555	374	1165 Grms.

The two fractions below 200° were distilled within 5°, and then within 2°, which brought together the following weights with smaller quantities at neighboring temperatures:—

96°-100°	116°-120°	136°-140°	148°-150°	158°-162°	168°-172°	190°-194°
34	25	35	40	60	20	40 Grms.

The lower portions of this oil began to come over at 45°, but only small quantities collected below 65°. At 65°-70°, 40 grms. collected, which will be examined in connection with the similar distillates from the other oils to ascertain whether the principal constituent is hexane or hexamethylene. The high specific gravity of this oil, even after treating thoroughly with fuming sulphuric acid, 0.7017, would seem to exclude hexane; specific gravity, 0.6671.

HEPTAMETHYLENE, C_7H_{14} .

The unpurified fraction 96°-100° gave as its specific gravity at 20°, 0.7395, and after treatment with fuming acid, 0.7384. The slight change in specific gravity indicates that this fraction consists for the most part of one hydrocarbon, and analysis with the boiling point shows that the hydrocarbon is heptamethylene; specific gravity, 0.7420:—

0.1473 grm. of the oil gave 0.4620 grm. CO_2 and 0.1879 grm. H_2O .

	Calculated for C_7H_{14} .	Found.
C	85.70	85.54
H	14.30	14.18

OCTONAPHTENE, C_8H_{16} .

The specific gravity of the fraction 116°-120° was 0.7625, and after treatment with fuming sulphuric acid, 0.7566, which indicated that this product contained very little of the benzol homologues. An analysis after purification gave proportions of carbon and hydrogen required for octonaphcene:—

0.1780 grm. of the oil gave 0.5572 grm. CO_2 and 0.2287 grm. H_2O .

	Calculated for C_8H_{16} .	Found.
C	85.70	85.39
H	14.30	14.28

FRACTION 150°-152°.

The distillates above 120° received no further attention, except to ascertain that the xylols were present in large proportion, as in the other oils. To ascertain whether nonane is contained in this oil, the specific gravity of the fraction 150°-152° was ascertained and found to be

0.7756, after treatment with the fuming acid. Its composition after treatment with the acid corresponded to that of C_nH_{2n} : —

0.1434 grm. of the oil have 0.4480 grm. CO_2 and 0.1839 grm. H_2O .

	Calculated for C_nH_{2n} .	Found.
C	85.70	85.20
H	14.30	14.25

The lower specific gravity of nonane and the results of analysis show that nonane is not a constituent of this oil.

DEKANAPHTENE, $C_{10}H_{20}$.

The specific gravity of the unpurified fraction 160° — 162° at 20° was 0.7966, and after purification with fuming sulphuric acid and sodic hydrate was 0.7905 ($C_{10}H_{20}$, 0.7950 at 0° Markownikoff).

It gave the following results on analysis : —

- I. 0.1471 grm. of the oil gave 0.4625 grm. CO_2 and 0.1907 grm. H_2O .
- II. 0.1475 grm. of the oil gave 0.4477 grm. CO_2 and 0.1813 grm. H_2O .

	Calculated for $C_{10}H_{20}$.	I.	Found. II.
C	85.70	85.50	85.86
H	14.30	14.37	14.17

On account of the small amount of the distillate 167° — 170° , no examination was made of it. It was doubtless chiefly a benzol homologue.

FRACTION 176° — 178 .

To ascertain whether a naphtene boiling at 182° is present in this oil, the fraction 176° — 178° was treated thoroughly with fuming sulphuric acid and sodic hydrate. Its specific gravity before treatment was 0.8116; after treatment, 0.7955. It gave on analysis 86.01 per cent carbon and 13.31 per cent hydrogen, indicating still the presence of a benzol homologue. But the small quantity remaining showed the absence of any other constituents with this boiling point in this distillate.

UNDEKANAPHTENE, $C_{11}H_{22}$.

The fraction 190° — 194° gave 0.8186 as its specific gravity before treatment with fuming sulphuric acid and sodic hydrate, and afterward, 0.8046. Markownikoff found 0.8119 at 0° as the specific gravity of dodekanaphtene from Baku oil.

The percentages of carbon and hydrogen given by analysis supported the formula of undekanaphtene:—

0.1466 grm. of the oil gave 0.4588 grm. CO₂ and 0.1909 grm. H₂O.

	Calculated for C ₁₁ H ₂₂ .	Found.
C	85.70	85.37
H	14.30	14.47

Some of the Bardsdale distillates, 140°–220°, 50 mm., turned pink soon after they were collected, changing to a darker red on standing, and after some time they deposited a dark oil. The colored distillates alternated with the others, leaving sharply lined uncolored oils beside those depositing the insoluble heavy oils. The following distillates were colored:—

154°–156°, 158°–160°, 168°–170°, 180°–182°, 198°–206°, 212°–216°.

The distillates between these were nearly or quite colorless. This coloration was caused by the phenol bodies, which are easily extracted by alkaline hydrates. The bodies will receive further attention in another paper.

ADAMS' CAÑON OIL.

The Adams' Cañon Oil from the Ex-Mission district was thicker and heavier than the oils previously described. The specific gravity of this specimen at 30° was 0.9212. It contained a large percentage of nitrogen, 1.46, determined by the volume of nitrogen. The Kjeldahl method gave 0.58 per cent. Two determinations of sulphur gave, (I.) 0.92, (II.) 0.87. This oil contained a very small proportion of the lower hydrocarbons. 100 grms. distilled under atmospheric pressure gave 8 grms. below 150°, and 27 grms., 150°–300°. The specific gravity of the lower distillate was 0.7673, and of the higher, 0.8457. In vacuum distillation, 9382 grms. of the crude oil gave the following weights:—

-150° At. Pr.	-120°	120°–160°	160°–250°
123	865	1045	525

Nearly three-fourths of the original oil remained above 250°.

Continuing the distillation of the lower distillates within 5° and 2°, the following weights were collected:—

96°–100°	116°–120°	158°–160°	168°–170°	180°–182°
37	10	12	20	10 Grms.

In continuing the distillation of the lower fractions nothing came over below 60°, and only in quantities of a few grams below 95°.

HEPTAMETHYLENE, C_7H_{14} .

The fraction 98°–100° unpurified gave as its specific gravity at 20°, 0.7444, and after treatment with fuming sulphuric acid and sodic hydrate, 0.7414. A combustion of the purified oil gave the following percentages of carbon and hydrogen: —

0.1525 grm. of the oil gave 0.4797 grm. CO_2 and 0.1976 grm. H_2O .

	Calculated for C_7H_{14} .	Found.
C	85.70	85.53
H	14.30	14.40

As in the other oils, much benzol was contained in the fractions near 80°, and toluol in those near 110°.

OCTONAPHTENE, C_8H_{16} .

The fraction 118°–120° gave as its specific gravity unpurified at 20°, 0.7632, and after treatment with fuming acid and sodic hydrate, 0.7600. Specific gravity of octonaphcene, 0.7582. This distillate gave after purification, 86.62 per cent of carbon, and 14.60 per cent of hydrogen, which with its boiling point showed it to be octonaphcene.

To ascertain whether nonane is a constituent of Adams' Cañon oil, the distillate 148°–150° was determined, and found to be 0.7858. After treatment with the fuming acid and sodic hydrate its specific gravity was but slightly changed, 0.7800. A combustion then gave 86.10 per cent of carbon, and 13.91 per cent of hydrogen.

Since nonane requires 84.37 per cent of carbon and 15.63 per cent of hydrogen, it is evident that this hydrocarbon is not a constituent of Adams' Cañon oil.

DEKANAPHTENE, $C_{10}H_{20}$.

The unpurified distillate 158°–160° gave as its specific gravity at 20°, 0.7972, and 0.7904 after treatment with the fuming acid and sodic hydrate. A combustion of the purified oil gave the following percentages of carbon and hydrogen: —

0.1455 grm. of the oil gave 0.4583 grm. CO_2 and 0.1804 grm. H_2O .

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.91
H	14.30	13.78

The low percentage of hydrogen and high percentage of carbon indicates that the benzol homologue was not completely removed. In some of these distillates, the benzol hydrocarbon is present in such large proportion that long continued action of the fuming acid is necessary to remove it completely.

The small amount of the distillate 180° - 182° gave as its specific gravity at 20° , 0.8154, and after treatment with the fuming acid, 0.8097. A combustion of the treated oil gave 85.56 per cent of carbon and 13.95 per cent of hydrogen. No further examination was made of the fractions collected under atmospheric pressure. Like the Bardsdale oil, part of the distillates between 140° and 220° under 50 mm. turned pink soon after they were collected, and on standing deposited a dark colored oil.

While the possibility of hydrocarbons poorer in hydrogen, such as condensed naphtene, is suggested by the low percentage of hydrogen, on account of the very large proportion of aromatic derivatives of benzol contained in Adams' Cañon oil, it seems more probable that these results are due to benzol derivatives not wholly removed, especially as the boiling points of the double ring naphtenes undoubtedly are much higher. Such a double ring naphtene apparently formed as one of the products by the action of sodium on monochlorheptamethylene boiled in the vicinity of 240° .

TORREY WELLS OIL.

The specimen of petroleum from the Torrey wells was much lighter than that from Adams' Cañon; its specific gravity at 20° was 0.8837. It contained 0.49 per cent of sulphur, and gave 0.38 per cent of nitrogen by the Kjeldahl method and 1.15 per cent by volume. A combustion gave 86.00 per cent of carbon, and 12.48 per cent of hydrogen; 100 grms. distilled under atmospheric pressure gave 11 grms. with a specific gravity 0.7519 below 150° , and 29 grms. specific gravity 0.8226 between 150° and 250° . In distilling Torrey oil *in vacuo*, 9860 grms. gave the following weights: —

-160° At. Pr.	-125°	125° - 175°	175° - 225°	225° - 275°
655	790	1175	900	700 Grms.

Further distillation of the lower fractions gave, after the fourth distillation, the following weights, with smaller proportions at temperatures between: —

96°-98°	116°-120°	136°-140°	158°-162°	168°-171°	178°-182°
78	40	45	37	43	35 Grms.

The Torrey oil contained more of the lower distillates than any other of the specimens examined. Several grams collected below 40°, and at 65°-70°, 30 grams came together. The unpurified distillate 65°-70° gave as its specific gravity at 50°, 0.6981, which was reduced only to 0.6926 after agitation with fuming sulphuric acid. The specific gravity of hexane boiling at 68° is 0.6630.

Analysis of the purified oil gave the following results:—

- I. 0.1551 grm. of the oil gave 0.4768 grm. CO₂ and 0.2138 grm. H₂O.
- II. 0.1995 grm. of the oil gave 0.6146 grm. CO₂ and 0.2769 grm. H₂O.
- III. 0.1369 grm. of the oil gave 0.4248 grm. CO₂ and 0.1888 grm. H₂O.

	Calculated for C ₆ H ₁₂ .	Calculated for C ₆ H ₁₄ .	I.	Found. II.	Found. III.
C	85.70	83.72	83.85	83.93	84.63
H	14.30	16.28	15.32	15.41	15.33

In analysis III. every precaution was taken to avoid loss of the oil after weighing, and the temperature of the combustion was maintained as high as the tube would stand. Probably the coincidence in the percentages of hydrogen is due to retention of unsaturated hydrocarbons in the sulphuric acid.

Apparently, as in the Fresno oil, the hydrocarbon at 68° is a mixture of hexane and hexamethylene.

HEPTAMETHYLENE, C₇H₁₄.

The fraction 96°-98° had the specific gravity at 20°, 0.7496, which was scarcely changed by treatment with fuming sulphuric acid, 0.7430. Analysis I. was made of the crude distillate, and analysis II. of the purified product:—

- I. 0.1222 grm. of the oil gave 0.3810 grm. CO₂ and 0.1602 grm. H₂O.
- II. 0.1530 grm. of the oil gave 0.4801 grm. CO₂ and 0.1974 grm. H₂O.

	Calculated for C ₇ H ₁₄ .	I.	Found. II.
C	85.70	84.97	85.60
H	14.30	14.56	14.34

This product is, therefore, fairly pure heptamethylene.

The fractions in the vicinity of 110° were shown to be composed for the most part of toluol by the formation of nitro-products.

OCTONAPHTENE, C_8H_{16} .

The specific gravity of the crude distillate 118° - 120° was 0.7598, and after purification with fuming sulphuric acid and sodic hydrate, 0.7530. A combustion of the unpurified oil gave 86.21 per cent of carbon and 13.35 per cent of hydrogen.

A combustion after purification indicated octonaphptene, although the percentage of hydrogen is somewhat too high, probably on account of accidental moisture:—

0.1470 grm. of the oil gave 0.4598 grm. CO_2 and 0.1976 grm. H_2O .

	Calculated for C_8H_{16} .	Found.
C	85.70	85.34
H	14.30	14.93

The distillates 135° - 140° consisted largely of the xylols.

DEKANAPHTENE, $C_{10}H_{20}$.

The specific gravity of the crude fraction 158° - 160° was 0.7742, and after purification with the fuming acid and sodic hydrate, 0.7742. Carbon and hydrogen were determined in the purified oil:—

0.1455 grm. of the oil gave 0.4583 grm. CO_2 and 0.1804 grm. H_2O .

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.91
H	14.30	13.78

The specific gravity of the crude distillate 168° - 170° was 0.7928, and 0.7840 after treatment with fuming acid and sodic hydrate. A combustion of the purified oil gave 85.98 per cent of carbon and 13.69 per cent of hydrogen.

The fraction 178° - 182° had the specific gravity before treatment, 0.8006, and afterward, 0.7924. A combustion of the oil after treatment gave 85.97 per cent of carbon and 13.51 per cent of hydrogen. The fraction 198° - 200° had the specific gravity of 0.8133, and after treatment, 0.8069. The following percentages of carbon were given by combustion: carbon, 86.51; hydrogen, 13.54.

The low proportions of hydrogen and high proportions of carbon alluded to before are especially apparent in the Torrey oil. Whether this be due to a higher series or to benzol homologues not easily

removed will appear later in the composition of the higher vacuum distillates.

The Torrey distillates 140°–220°, 50 mm., showed a larger proportion of oxygen and nitrogen compounds than any other of the crude oils.

SCOTT'S HILL (SESPE DISTRICT) OIL.

The specimen of petroleum from Scott's Hill was lighter than the Torrey oil; its specific gravity at 20° was 0.8782. It contained 1.25 per cent of nitrogen. Two determinations of sulphur gave (I.) 0.38 and (II.) 0.49 per cent. 8260 grms. of the crude oil gave the following weights on distillation *in vacuo* :—

-150° At. Pr.	-160°	160°–208°	208°–275°
1220	495	930	880

The distillate -150° was collected under atmospheric pressure, the others under 70 mm. The portion -150° was subjected to further distillation collecting at first within 5°, and twice within 2°. The fractions collected in larger quantities within the following limits :—

66°–70°	86°–90°	96°–100°	116°–120°	136°–140°	156°–160°	170°–174°	178°–182°	190°–192°
26	38	35	37	38	62	41	38	41

Continuing the distillation of the higher fractions *in vacuo*, after the third distillation within limits of 2°, the larger quantities collected within the following limits with smaller quantities between :—

144°–148°	164°–168°	182°–186°	210°–214°
60	55	65	23

In distilling corresponding fractions from other fields *in vacuo* a tendency to collect within the same limits was observed. After agitation with fuming sulphuric acid, the fraction 66°–70° atmospheric pressure gave as its specific gravity at 20°, 0.6984; the specific value much higher than the specific gravity of hexane, 0.6630(17°5). A combustion gave percentages of carbon and hydrogen corresponding to a mixture of hexamethylene and hexane :—

	Calculated for		Found
	C ₆ H ₁₂ .	C ₆ H ₁₄ .	
C	85.70	83.72	84.67
H.	14.30	16.28	15.15

The distillates 65°–70° from Torrey, Scott's Hill, and Fresno oils were put together and carefully distilled a number of times in order to separate so far as possible the hydrocarbon boiling at 68° or 69° from other admixtures, and the fraction 68°–69° was thoroughly treated with fuming sulphuric acid, warming gently and allowing it to stand with the acid over night. Before treatment the specific gravity at 20° was 0.7005, and after treatment, 0.6929. The following results were obtained by analysis: —

I. 0.2422 grm. of the oil gave 0.7596 grm. CO₂ and 0.3234 grm. H₂O.

	Calculated for		Found. I.
	C ₆ H ₁₂ .	C ₆ H ₁₄ .	
C	85.70	83.72	85.50
H	14.30	16.28	14.84

In this analysis the combustion tube was filled with oxygen before the oil was volatilized, and the temperature was kept as high as the tube would stand. There seems therefore to be little doubt that the hydrocarbon in California petroleum boiling at 68°–69° is composed chiefly of hexamethylene.

Since small quantities of distillates remained in the vicinity of 90°–91°, it suggested the possibility that isoheptane might form a part of this product. But its high specific gravity, 0.7303 at 20°, isoheptane 0.6819 (17°.5), and the composition showed by analysis, excluded isoheptane in any considerable quantity.

0.1273 grm. of the oil gave 0.3987 grm. CO₂ and 0.1665 grm. H₂O.

	Calculated for		Found.
	C ₇ H ₁₄ .	C ₇ H ₁₆ .	
C	85.70	84.00	85.40
H	14.30	16.00	14.53

Especial precautions were taken in this analysis to have the temperature of the combustion as hot as possible, and the tube was filled with oxygen before the oil volatilized. The proportions of carbon and hydrogen indicating the absence of isoheptane could not have been due to the presence of benzol, since the oil was treated several times with fuming sulphuric acid. The volatile portions of California petroleum, therefore, contain at most very small proportions of the hydrocarbons, C_nH_{2n+2}, and these if present consist almost exclusively of members below normal hexane. Further confirmation of these formulae is given by the chlorine derivatives, which will be described in another paper.

HEPTAMETHYLENE, C_7H_{14} .

The fraction 96° — 98° gave as its specific gravity at 20° , 0.7479, and after purification with fuming sulphuric acid, 0.7436. A combustion of the purified oil gave the following results: —

0.1530 grm. of the oil gave 0.4801 grm. CO_2 and 0.1974 grm. H_2O .

	Calculated for C_7H_{14} .	Found.
C	85.70	85.60
H	14.30	14.34

These values leave no doubt that this constituent was heptamethylene.

OCTONAPHTENE, C_8H_{16} .

A determination of the specific gravity of the fraction 118° — 120° at 20° gave 0.7628, and after agitation with fuming acid and sodic hydrate, 0.7569. Determinations of carbon and hydrogen were made both before and after purification.

I. 0.1644 grm. of the unpurified oil gave 0.5196 grm. CO_2 and 0.1975 H_2O .
 II. 0.1470 grm. of the purified oil gave 0.4600 grm. CO_2 and 0.1976 grm. H_2O .

	Calculated for C_8H_{16} .	Found.	
		I.	II.
C	85.70	86.21	85.34
H	14.30	13.35	14.93

Although all these oils were dried over sodium, the hydrogen in analysis II. is somewhat too high, probably on account of a trace of moisture.

No further examination of the higher fractions of this oil below 160° was made, except of the portions collected at 135° — 140° , to show that large proportions of the xylols were contained as in the other specimens examined.

DEKANAPHTENE, $C_{10}H_{20}$.

The specific gravity of the fraction 158° — 160° was found to be 0.7848, and after agitation with the fuming acid, 0.7751. The proportions of carbon and hydrogen were determined by analysis: —

I. 0.1444 grm. of the oil gave 0.4575 grm. CO₂ and 0.1885 grm. H₂O.
 II. 0.1451 grm. of the oil gave 0.4533 grm. CO₂ and 0.1848 grm. H₂O.

	Calculated for C ₁₀ H ₂₀ .	Found.	
I.	II.		
C	85.70	85.65	85.24
H	14.30	14.22	14.33

UNDEKANAPHTENE, C₁₁H₂₂.

The specific gravity of this fraction without purification was 0.8093 at 20°, and after treatment with the fuming acid and sodic hydrate, 0.7952. A combustion gave the following percentages of carbon and hydrogen:—

0.1458 grm. of the oil gave 0.4593 grm. CO₂ and 0.1817 grm. H₂O.

	Calculated for C ₁₁ H ₂₂ .	Found.
C	85.70	85.90
H	14.30	13.85

Assuming, which is probable, that the benzol homologue was completely removed, these proportions of carbon and hydrogen point to the presence of a hydrocarbon of a series containing less hydrogen.

A similar result was obtained with the fraction 194°–196°, specific gravity crude, 0.8145, and after treatment, 0.8022. Combustion of the purified oil gave the following percentages:—

	I.	II.
C	85.52	85.85
H	13.97	13.92

While the percentages of carbon in these analyses are satisfactory for the formula C_nH_{2n}, the percentages of hydrogen are less satisfactory. The deficiency of about one half of one per cent in the sum of the carbon and hydrogen has appeared in many of the analyses of products that could be reasonably accepted as to their formula. With the greatest care in the details of analysis, we have also found difficulty in obtaining the total carbonic dioxide evolved by combustion of the oil in the ordinary method of analysis. This subject has received attention in another paper on this method of analysis.

TRIDEKANAPHTENE, C₁₃H₂₆.

After the separation of distillates *in vacuo* from the crude oils, the fractions may be distilled at temperatures which would cause decomposi-

tion of constituents of the crude oil. It is therefore possible to continue the distillation of the hydrocarbons even as high as tridekanaphtene under atmospheric pressure after the first distillation. In continuing the distillation, 35 grams collected at 230°-232°, specific gravity 0.8511. After purification with fuming sulphuric acid it gave as its specific gravity 0.8134 at 20°. A combustion gave the following results:—

0.1511 grm. of the oil gave 0.4733 grm. CO₂ and 0.1937 grm. H₂O.

	Calculated for C ₁₃ H ₂₆ .	Found.
C	85.70	85.41
H	14.30	14.24

This formula was also verified by a determination of its molecular weight:—

1.2712 grm. of the oil and 25.24 grms. benzol gave a depression of 1°.370.

	Calculated for C ₁₃ H ₂₆ .	Found.
	182	180

A determination of the index of refraction gave 1.4745, and the molecular refraction 60.254; calculated for C₁₃H₂₆, 59.839.

TETRADEKANAPHTENE, C₁₄H₂₈.

A considerable quantity of distillate collected at 144°-146°, which gave as its specific gravity before purification 0.8428, and after purification 0.8154. A combustion gave percentages of carbon and hydrogen required for the formula C_nH_{2n}.

0.1462 grm. of the oil gave 0.4600 grm. CO₂ and 0.1824 grm. H₂O.

	Calculated for C _n H _{2n} .	Found.
C	85.70	85.81
H	14.30	13.87

A determination of molecular weight at the freezing point gave a value required for tetradekanaphtene:—

1.3356 grm. of the oil and 24.22 grms. benzol gave a depression of 1°.394.

	Calculated for C ₁₄ H ₂₈ .	Found.
	196	194

The index of refraction of this hydrocarbon was found to be 1.4423, and the molecular refraction 63.75; required for C₁₄H₂₈, 64.44.

PENTADEKANAPHTENE, $C_{15}H_{30}$.

From each of the California oils, distillates *in vacuo* collected at 160° – 162° , 50 mm., corresponding nearly to 260° – 262° , atmospheric pressure. The specific gravity of the fraction from Scott's Hill oil was 0.8600, and after purification with fuming sulphuric acid, 0.8171. A combustion gave the following values for carbon and hydrogen:—

0.1454 grm. of the oil gave 0.4558 grm. CO_2 and 0.1829 grm. H_2O .

	Calculated for $C_{15}H_{30}$.	Found.
C	85.70	85.47
H	14.30	13.97

The percentages of carbon and hydrogen in the analysis of the two hydrocarbons last described indicate a falling off in the proportions of hydrogen. The deficiency in the analysis is more probably due to loss of carbonic dioxide than of water. Similar variations have been noted in connection with some of the lower hydrocarbons in other crude California oils. The deficiency in hydrogen may indicate, as mentioned heretofore, the presence of hydrocarbons composed with more than one methylene ring, which would require prolonged distillation for their complete removal. From the heavier California oils composed, it appears, largely of asphaltic hydrocarbons, the falling off in the proportion of hydrogen and consequent increase in carbon indicates the presence of hydrocarbons with the formula C_nH_{2n-2} . Such differences do not appear in determinations of molecular weights, but are shown by analysis.

There are wide variations in the specific gravity of the distillates of California oil above 230° from different sources. This may indicate a certain proportion of hydrocarbons of a lower series than C_nH_{2n} , and the higher percentages of carbon and lower percentages of hydrogen in some of these oils indicate the possibility of hydrocarbons C_nH_{2n-2} .

For faithful assistance in this work the following gentlemen should receive credit: Messrs. Shaw, Ames, Richards, Cushing.

From this examination of California petroleum, the following conclusions may be drawn:—

An essential characteristic is the relatively small proportions of the distillates below 225° . The main body of the crude oils from the principal fields distilling below 225° is composed of methylenes which resemble those identified in Russian oil, in boiling points and in specific gravity, except undekanaphtene, $C_{11}H_{22}$, dodekanaphtene, $C_{12}H_{24}$, and tridekanaphtene, $C_{13}H_{26}$, which differ in boiling points. The proportion of the

aromatic hydrocarbons is much larger, apparently, in California oil. The homologues of benzol form a considerable proportion of the distillates, especially of those with lower boiling points. In the distillate 221°-222° from Puente oil so much naphtalene was present that the distillate became solid at 0°.

California petroleum differs totally from the Eastern oils,—Pennsylvania, Ohio, Canadian, etc.,—and also materially from Russian oil, in not containing members of the series C_nH_{2n+2} . In this respect, and in respect to the large proportion of aromatic hydrocarbons, California petroleum is unlike any other petroleum that has been examined in this Laboratory. Incidentally it may be mentioned that California petroleum differs from other petroleums hitherto examined in the large proportions of oxygen and nitrogen compounds which it contains. These bodies are under investigation in this Laboratory.

Study of the portions with high boiling points, which is now in progress, will have an especial interest, since, when they are separated without decomposition, they form the most valuable constituents of lubricating oils and asphalts that have been separated from petroleum. In some of the high distillates, such as those from Summerland oil, hydrocarbons of the series C_nH_{2n-2} and the series C_nH_{2n-4} have been identified.

No. 36.—ON THE CHLORINE DERIVATIVES OF THE HYDROCARBONS IN CALIFORNIA PETROLEUM.

By CHARLES F. MABERY AND OTTO J. SIEPLEIN.

IN further confirmation of the composition of the hydrocarbon 68°-70° described in the previous paper (Mabery and Hudson), the chlorine derivatives were formed by exposing the hydrocarbon over water to the action of chlorine, in ordinary daylight. After washing and drying, the chlorine product was fractionated under atmospheric pressure until it collected at 125°-130°, and for the most part at 126°. It distilled constant under normal conditions with the mercury all in the vapor at 125°.5.

The specific gravity at $\frac{20}{20}$ ° was 0.9255; at $\frac{20}{40}$ °, 0.9239; at $\frac{30}{40}$ °, 0.9143; and at $\frac{40}{40}$ °, 0.9044. The coefficient of expansion calculated from the average of these determinations is 0.000918.

A chlorine determination gave the following percentage: —

0.1572 grm. of the oil gave 0.1872 grm. AgCl.

	Calculated for C ₆ H ₁₁ Cl.	Found.
Cl	29.92	29.50

The molecular weight was determined at the freezing point of benzol. 1.1641 grm. of the oil and 19.92 grm. benzol gave a depression of 2°.482.

	Calculated for C ₆ H ₁₁ Cl.	Found.
	118.5	118

The index of refraction at 20° was found to be 1.416, and the molecular refraction, 33.29. Required for C₆H₁₁Cl, 32.54. Hexamethylene is, therefore, the principal hydrocarbon with this boiling point.

In distilling the portions of California petroleum below 100°, it has always been observed that a distillate collected at 90°-91°. To ascertain whether a hydrocarbon were really present with this boiling point, distillation of the fractions 85°-100° was continued through a tall Hempel column until a larger portion collected at 89°-90°. The specific gravity of this fraction without purification was 0.7295, $\frac{20}{20}$. After thorough treatment first with common sulphuric acid, then with fuming acid, the specific gravity was not changed, 0.7295. The index of refraction of this hydrocarbon at 20° was 1.411, and the molecular refraction 33.35; calculated for C₇H₁₄, 32.22. The molecular weight at the freezing point was found to be as follows: —

0.8669 grm. of the oil and 17.62 grms. of benzol gave a depression 2°.547.

	Calculated for C ₇ H ₁₄ .	Found.
	98	99

With the mercury column all in the vapor, Bar. 745.3 mm., this hydrocarbon distilled completely at 90°.4.

The chlorine derivative of this hydrocarbon was formed by the action of chlorine over water. After washing, drying, and distillation under atmospheric pressure, the chloride came together at 145°-150°, for the most part at 147°.

A determination of chlorine gave a value required for the monochloride: —

0.1605 grm. of the oil gave 0.1696 grm. AgCl.

	Calculated for C ₇ H ₁₃ Cl.	Found.
Cl	26.77	26.13

The specific gravity of the chloride at $\frac{20}{20}$ was 0.9332; at $\frac{20}{40}$, 0.9316; at $\frac{30}{40}$, 0.9231; at $\frac{40}{40}$, 0.9138. The coefficient of expansion for one degree calculated from these results is 0.000973.

A determination of the molecular weight at the freezing point gave the following value:—

0.9318 grm. of the oil and 19.98 grms. of benzol gave a depression of $1^{\circ}.744$.

Calculated for C ₇ H ₁₃ Cl.	Found.
132.5	131

The index of refraction at 20° was found to be 1.441, and the molecular refraction, 37.57; calculated for C₇H₁₃Cl, 37.11.

These results are sufficient to establish the formula for this hydrocarbon as C₇H₁₄. It is probably dimethylpentamethylene. It differs in its properties from methylhexamethylene, boiling point 99°–100°; its chloride boils at 147°, while methylhexamethylene chloride boils at 141°–142°.

METHYLHEXAMETHYLENE CHLORIDE, C₇H₁₃Cl.

To ascertain the correct boiling point of heptamethylene, the distillates 95°–100° were carried through a series of distillations until the greater portion collected at 98°–100°, and this product distilled for the most part at 99°–100°, Bar. 745°.3, with the mercury column wholly in the vapor.

The empirical formula of this hydrocarbon has been ascertained in the distillates from various specimens of California oils, by analysis and determinations of molecular weight. The boiling point of hexahydrotoluol, prepared by the addition of hydrogen to toluol, was given as 97°. Markownikoff found that the same hydrocarbon separated from Russian petroleum, and also the synthetically prepared heptanaphthene, boiled at 101°.

For further identification of our product it seemed advisable to study its derivatives. The chlorine derivative was first formed by passing chlorine into the hydrocarbon over water until the greater part was converted into the chloride. This reaction takes place very readily in

ordinary daylight, and with a large generator the action of chlorine may be made continuous, saving much time in the chlorination. This method seems to be more advantageous than that formerly used by us in which dry chlorine was allowed to act on the vapor of the dry oil. The chlorinated oil was washed, dried over calcium chloride, and fractionated. After five distillations through a Hempel column, a considerable portion collected at 141°-142°, which proved to be the monochloride, and more remained above 160°, which was doubtless the dichloride.

A determination of chlorine in the fraction 141°-142° by the method of Carius gave a value required for $C_7H_{13}Cl$: —

0.1863 grm. of the oil gave 0.2025 grm. $AgCl$.

	Calculated for $C_7H_{13}Cl$.	Found.
Cl	26.77	26.88

The molecular weight was also determined by the Beckman freezing point method: —

1.1960 grm. of the oil and 25.8960 grms. benzol gave a depression of 1°.701.

	Calculated for $C_7H_{13}Cl$.	Found.
	132.5	133

The specific gravity of the monochloride at 20° was found to be 0.9310. For further confirmation of the formula, the index of refraction was determined with the aid of a Pulfrich refractometer, and from the density and molecular weight the molecular refraction was calculated. The index of refraction found was 1.441, and the molecular refraction: —

	Calculated for $C_7H_{13}Cl$.	Found.
	37.11	37.57

The theoretical value was calculated on the assumption that all the carbons are singly connected.

In order to ascertain whether the chlorine atom enters the ring or side chain, the nitril was formed by heating the chloride with alcoholic potassic cyanide for several hours. There was an abundant separation of potassic chloride, and on diluting the solution the nitril separated as an oily liquid above the water. This oil had the characteristic odor of the nitrils. Its specific gravity at 20° was 0.9253, and its index of refraction, 1.45. The molecular refraction, assuming the molecular weight, was

35.78, calculated from the elements, assigning to the cyanogen group the value 5.33, which was determined from ethyl cyanide, C_2H_5CN . The theoretical molecular refraction for the nitril calculated on the same basis is 36.45.

The nitril was saponified by heating it to 110° with concentrated hydrochloric acid. The acid formed had the odor of alphatoluic acid, but the amount obtained was not sufficient for complete examination.

When heptamethylene chloride was brought together with metallic sodium, a vigorous action soon set in with the evolution of great heat, sufficient to cause the decomposition of the products unless it was controlled by cooling. This reaction was best carried on by dissolving the chloride in ether, adding the sodium in slight excess over the calculated amount, and keeping the solution cold. In two hours the reaction was complete. The products included an unsaturated hydrocarbon, boiling point 97° , and another hydrocarbon, boiling point approximately 220° — 230° . That the hydrocarbon boiling at 97° was unsaturated was shown by the formation of a bromine addition product; bromine added readily in the cold with no escape of hydrobromic acid. A Carius determination of the bromine in this product gave the following result: —

0.2045 grm. of the oil gave 0.3023 grm. $AgBr$.

	Calculated for $C_7H_{12}Br_2$.	Found.
Br	62.5	62.9

The specific gravity of the dibrom-derivative at 20° was 1.648. A determination of its molecular weight was made: —

0.9238 grm. of the oil and 25.3 grms. of benzol gave a depression of $0^\circ.725$.

	Calculated for $C_7H_{12}Br_2$.	Found.
	256	247

The odor of the unsaturated hydrocarbon was very sharp and penetrating, very different from that of the paraffine and methylene hydrocarbons, but resembling the olefines. In further proof that it contained doubly bonded carbon, it was titrated with the Hübl reagent, an alcoholic solution of iodine and mercuric chloride. The amount of iodine absorbed was approximately equivalent to two atoms of iodine for each molecule of the hydrocarbon. When heated with hydriodic acid, the monoiodide was readily formed. The specific gravity of the unsaturated hydrocarbon

at 20° was 0.7472. Its molecular weight was ascertained by the freezing point method : —

0.7116 grm. of the oil and 25.19 grms. of benzol gave a depression of 1.420.

Calculated for C ₇ H ₁₂ .	Found.
96	98

The index of refraction with sodium light was found to be 1.416. The molecular refraction calculated from the density and molecular weight was : —

C ₆ H ₉ CH ₃ .	Calculated for C ₆ H ₁₀ =CH ₂ .	Found.
30.06	31.77	32.34

These values indicate that the unsaturated hydrocarbon contains a double bond between the side chain carbon and a carbon atom in the ring, confirming the position of the chlorine atom in the side chain which is indicated by the ease with which it is replaced in the reaction with potassic cyanide. The form that the chlorination takes doubtless depends on the fact that the hydrogen in the side chain is less firmly bound than the hydrogen atoms in the methylene ring. The unsaturated condition C₆H₁₀=CH₂ is shown by the action of halogens and haloid acids, and confirmed by the molecular refraction, which corresponds to the sum of the atomic refractions assuming the double bond.

This constituent of California petroleum is therefore identical with methyl hexamethylene, which may be formed by the addition of hydrogen to toluol.

The hydrocarbon with a boiling point 220°-230°, formed by the action of sodium on methyl hexamethylene chloride, doubtless contains two methylene rings : — C₆H₁₁CH₂-CH₂C₆-H₁₁. The quantity of this product formed was too small for identification, but it evidently affords a means for building up the higher methylene hydrocarbons containing more than one methylene ring. That it was a condensed hydrocarbon was shown by its high specific gravity, 0.8872.

DIMETHYLHEXAMETHYLENE CHLORIDE, C₈H₁₅Cl.

The formula of dimethylhexamethylene was ascertained, as shown in the previous paper, by analysis and determination of its molecular weight. The formula was still further verified by the formation of the chlorine derivative. As in the chlorination of methylhexamethylene, chlorine

was allowed to act on the hydrocarbon over water in ordinary daylight until it was nearly all converted into the chlorine derivative. After washing and drying, the product was distilled under atmospheric pressure; after several distillations the monochloride collected in larger part at 168°–170°. The specific gravity of this product at 20° was found to be 0.9358. A determination of chlorine gave the following result:—

0.2034 grm. of the oil gave 0.1973 grm. AgCl.

	Calculated for C ₈ H ₁₅ Cl.	Found.
Cl	24.21	24.01

The molecular weight of the chloride was determined by the freezing point method.

0.7293 grm. of the oil and 25.66 grms. benzol gave a depression of 0°.982.

	Calculated for C ₈ H ₁₅ Cl.	Found.
	146.5	142

The index of refraction in sodium light at 20° was 1.455, and the molecular refraction:—

	Calculated for C ₈ H ₁₅ Cl.	Found.
	41.69	41.60

That the chlorine enters a side chain in this reaction, as in the case of methylhexamethylene, appears from the ready formation of the nitril by heating the chloride with alcoholic potassic cyanide. On diluting the solution the nitril separated as an oil, with the characteristic odor of the nitrils. It was saponified by heating with aqueous potassic hydrate. On acidifying the solution, a solid was precipitated, with an odor characteristic of the alpha-tolueic acids; but the quantity obtained was not sufficient for identification. It was probably meta-methyl, alpha-toluylic acid.

TRIMETHYLHEXAMETHYLENE CHLORIDE, C₉H₁₇Cl.

This chloride was also formed, washed, dried, and fractioned under atmospheric pressure. It came together in larger quantity at 186°–188°; its specific gravity at 20° was 0.9380. The percentage of chlorine was determined.

0.2300 grm. of the oil gave 0.2041 grm. AgCl.

	Calculated for C ₉ H ₁₇ Cl.	Found.
Cl	22.10	21.94

The molecular weight was also ascertained at the freezing point.

0.8672 grm. of the oil and 25.03 grms. benzol gave a depression of $1^{\circ}.090$.

Calculated for $C_9H_{17}Cl$.	Found.
160.5	156

In further support of the formula of the chloride, the index of refraction was determined, 1.462, and the molecular refraction calculated.

Calculated for $C_9H_{17}Cl$.	Found.
46.3	47

When sodium was allowed to act on trimethylhexamethylene chloride, a vigorous reaction set in that could be controlled by cooling. By carrying on the reaction in an ethereal solution, on standing over night in water the reaction was complete. The product of the reaction consisted for the most part of an unsaturated hydrocarbon, and a smaller quantity of a heavy oil, doubtless formed by the union of two methylene rings. The boiling point of the unsaturated hydrocarbon was 135° – 140° . Its unsaturated condition was shown by the readiness with which it united with iodine in Hübl's reagent, absorbing approximately two atoms of iodine. The specific gravity of the unsaturated hydrocarbon at 20° was 0.7762. The molecular weight at the freezing point was determined.

0.8572 grm. of the oil and 22.45 grms. benzol gave a depression of $1^{\circ}.571$.

Calculated for C_9H_{16} .	Found.
124	120

The index of refraction was found to be 1.431, and the molecular refraction:—

$C_8H_7(CH_3)_3$.	Calculated for $C_8H_8(CH_3)_2=CH_2$.	Found.
39.26	40.97	41.46

DEKANAPHTENE CHLORIDE, $C_{10}H_{19}Cl$.

In confirmation of the formula of dekanaphtene, the index of refraction was determined and the molecular refraction calculated. With the density 0.7898, and the index 1.4325, the molecular weight gave the following value:—

Calculated for $C_{10}H_{20}$.	Found.
46.10	46.00

The chlorine derivative of this hydrocarbon was formed by passing in chlorine over water. After washing, drying, and fractioning *in vacuo*, the chloride collected in larger quantities at 105°–110° (50 mm.). Another portion collected at 140°–145°, probably a dichloride. The specific gravity of the monochloride at 20° was 0.9470. A determination of chlorine gave the following value: —

0.1840 grm. of the oil gave 0.1476 grm. AgCl.

	Calculated for C ₁₀ H ₁₉ Cl.	Found.
Cl	20.33	19.80

The molecular weight of the chloride at the freezing point of benzol was also determined: —

1.2536 grm. of the oil and 21.29 grms. benzol gave a depression of 1°.689.

	Calculated for C ₁₀ H ₁₉ Cl.	Found.
	174.5	171

A determination of the index of refraction of this chloride gave 1.468. The molecular refraction calculated as follows: —

	Calculated for C ₁₀ H ₁₉ Cl.	Found.
	50.89	51.34

On account of the small quantity of the dichloride obtained, it was not possible to purify it completely by distillation. But a determination of chlorine gave 31.53 per cent; required for C₁₀H₁₈Cl₂, 33.90. A determination of molecular weight gave 199; required for the dichloride, 209. The molecular refraction calculated from the index was 56.98; calculated from the formula, 55.81. On account of the differences between the theoretical values for the mono- and di-chlorides, these values are sufficient to show that the dichloride was formed and separated in nearly a pure form.

UNDEKANAPHTENE CHLORIDE, C₁₁H₂₁Cl.

The index of refraction of this hydrocarbon was found to be 1.4403, and the molecular refraction: —

	Calculated for C ₁₁ H ₂₂ .	Found.
	50.70	50.63

This determination was made in the distillate 190°–192°, which was used for all work on this hydrocarbon.

The chlorine derivative was prepared in the same manner as those of the hydrocarbons previously described. On fractioning it *in vacuo* at 35 mm. it collected for the most part at 125°–130°. Its specific gravity was found to be 0.9583 at 20°. A chlorine determination supported the formula of the monochloride.

0.1560 grm. of the oil gave 0.1179 grm. AgCl.

Calculated for C ₁₁ H ₂₁ Cl.	Found.
18.81	18.69

The molecular weight was determined at the freezing point of benzol.

0.6055 grm. of the oil and 17.37 benzol gave a depression of 0°.890.

Calculated for C ₁₁ H ₂₁ Cl.	Found.
188.5	192

The index of refraction was found to be 1.476, and the molecular refraction:—

Calculated for C ₁₁ H ₂₁ Cl.	Found.
55.48	54.82

The composition of its chloride, together with its molecular weight and molecular refraction, all show that undecane has for its boiling point 194°–196°.

DODEKANAPHTENE CHLORIDE, C₁₂H₂₃Cl.

The index of refraction of dodekanaphtene was found to be 1.4649, and the molecular refraction:—

Calculated for C ₁₂ H ₂₄ .	Found.
55.38	55.24

The chlorine derivative was formed, washed, dried, and fractioned *in vacuo*. It collected for the most part at 130°–135° (17 mm.) Its specific gravity at 20° was 0.9616. A determination of chlorine gave the following result:—

0.1657 grm. of the oil gave 0.1153 grm. AgCl.

Calculated for C ₁₂ H ₂₃ Cl.	Found.
Cl	17.52

The molecular weight was also determined:—

0.7172 grm. of the oil and 19.04 grms. benzol gave a depression of 0.925.

Calculated for $C_{12}H_{28}Cl$.	Found.
202.5	204

The index of refraction was 1.480, and the molecular refraction:—

Calculated for $C_{12}H_{28}Cl$.	Found.
60.77	59.96

TRIDEKANAPHTENE CHLORIDE $C_{13}H_{25}Cl$.

The index of refraction of this hydrocarbon as determined is 1.4745, and its molecular refraction:—

Calculated for $C_{13}H_{26}$.	Found.
60.25	59.84

The chlorine derivative was formed by the action of chlorine, dried and fractioned under 17 mm.; it came together for the most part at 140°–145°. Its specific gravity at 20° was 0.9747; a Carius determination gave the following percentage of chlorine:—

0.1674 grm. of the oil gave 0.1137 grm. $AgCl$.

Calculated for $C_{13}H_{25}Cl$.	Found.
16.38	16.78

In the chlorine derivatives of the higher hydrocarbons the weight of oil that can be taken for analysis is limited, since as in the last analysis the pressure of the large volume of gases formed is more than the tube can stand. The molecular weight of tridekanaphtene chloride was determined at the freezing point of benzol:—

0.4447 grm. of the oil and 17.88 grms. benzol gave a depression of 0.763.

Calculated for $C_{13}H_{25}Cl$.	Found.
216.5	217

TETRADEKANAPHTENE CHLORIDE, $C_{14}H_{27}Cl$.

Tetradekanaphtene chloride was readily formed by passing chlorine into the hydrocarbon over water in ordinary daylight; if the action was stopped with a small portion of the hydrocarbon unacted on, the product consisted for the larger part of the monochloride. After washing and drying, the chlorine derivative was separated by continued distillation *in*

vacuo under 13 mm. ; it came together for the most part at 150°–155°. The specific gravity of the monochloride was 0.9748 $\frac{20}{20}$; at $\frac{20}{40}$ 0.9730 ; at $\frac{20}{40}$, 0.9661 ; and at $\frac{40}{40}$, 0.9579. The mean coefficient of expansion, within 20°–40°, from these results, is 0.00078.

A determination of chlorine gave a value required for the monochloride:—

0.1559 grm. of the oil gave 0.0989 grm. AgCl.

	Calculated for C ₁₄ H ₂₇ Cl.	Found.
Cl	15.39	15.80

As mentioned above, the decreasing proportion of chlorine in these derivatives with the increasing molecular weight, and the consequent larger volumes of gases, beyond the strength of the ordinary Carius tubes, gives a smaller weight of silver chloride than could be desired, but the accuracy of the method permits of sufficiently reliable results, even with the small weights.

The molecular weight of the chloride was determined at the freezing point of benzol :—

0.8923 grm. of the oil and 17.76 grms. benzol gave a depression of 1°.094.

	Calculated for C ₁₄ H ₂₇ Cl.	Found.
	230.5	225

The index of refraction was found to be, 1.493, and the molecular refraction 68.67 ; calculated for C₁₄H₂₇Cl, 69.37.

The boiling point of this chloride cannot be accurately determined under atmospheric pressure because it is rapidly decomposed at the higher temperature and in presence of air, although it may be distilled indefinitely *in vacuo*. Probably the boiling point under atmospheric pressure is not far from 275°.

PENTADEKANAPHTENE CHLORIDE, C₁₅H₂₉Cl.

This chloride was prepared from pentadekanaphtene, which had been well fractioned *in vacuo*. These higher chlorides are formed as readily as the lower ones. After washing and fractional distillation under 14 mm. this monochloride came together for the most part at 170°–175° without decomposition. Its boiling point under atmospheric pressure is probably near 300°. Its specific gravity at $\frac{20}{20}$ was 0.9771 ; at $\frac{20}{40}$ 0.9753 ; and at $\frac{30}{40}$, 0.9714 ; and at $\frac{40}{40}$, 0.9643. The coefficient of expansion calcu-

lated from these values is 0.000576. A Carius determination gave the required percentage of chlorine.

0.1536 grm. of the oil gave 0.0923 grm. silver chloride.

Calculated for C ₁₅ H ₂₉ Cl.	Found.
14.51	14.85

A determination of the molecular weight supported the same formula.

0.9073 grm. of the oil and 18.93 grms. benzol gave a depression of 0°.984.

Calculated for C ₁₅ H ₂₉ Cl.	Found.
239	244.5

The index of refraction was 1.493, and the molecular refraction, 72.90; calculated for C₁₅H₂₉Cl, 73.97.

Attempts will be made to form the chlorides of the higher hydrocarbons in connection with the study of the composition of these bodies.

No. 37.—ON THE COMPOSITION OF JAPANESE PETROLEUM.

BY CHARLES F. MABERY AND SHINICHI TAKANO.*

THE oil fields in Japan are the most promising and are under the most rapid development of any recently discovered oil territory. The output in 1891 was 56,000 bbls. annually; in 1899 it was 1,000,000 bbls. The oil territory in Japan is contained in the province of Echigo, at least to the extent of 90 per cent, on the northern coast of the Sea of Japan. This province is surrounded in part by a mountain chain which

* Mr. Takano has spent three years in the study of petroleum in this country, having been sent for this purpose by the Japanese Government. He is thoroughly familiar with the geology of the oil territory in Japan, having given especial attention to this subject in a thesis which he presented for a degree in the University of Tokio. Besides a thorough knowledge of the composition of petroleum from a chemical point of view, which he has gained during the two years he has spent exclusively in the study of this subject in this Laboratory, Mr. Takano spent one year as a laboree in different refineries, where he took charge by actual manipulation of every process in the preparation of commercial products. The work presented in this paper formed the subject of a thesis by Mr. Takano for the degree of M.S.

encloses a section of country 140 miles long by 150 miles broad, rising gradually from the sea to the mountains with a varying altitude from 150 feet to 500 feet. Oil is found chiefly in the Upper Eocene of the Tertiary formation, where it is held under pressure between impervious layers of slate and sandstone.

Nodules of calcite are frequently found embedded in the sandstone, and crystals of calcite twinned, resembling those found in the Ohio Trenton-limestone, oil-bearing rock. The oil strata are full of sea-shells, a good indication as to the origin of the oil formations. There are great variations in the depths of the wells. For example, the wells of the Amaze field are approximately 2000 feet in depth, while those of the Miyagawa field, only six miles distant, are 700 feet deep; the wells of the Niitsu field are still shallower, 600 feet. The Nagaoka wells are 800 feet in depth. Nevertheless the oil strata at the different depths are essentially of the same formation. The sandstone in which the Nagaoka oil is found is coarser than that of the other fields. On the surface of the Niitsu oil territory are immense beds of peat which are used for fuel.

Although the oil fields of Japan are situated in close proximity, specimens of oil from the different fields differ as essentially in composition as the variations in specific gravity indicate. As will appear later, the Amaze, Miyagawa, and Hirei fields yield paraffine in considerable quantities. While the hydrocarbons above C_7H_{14} do not include members of the series C_nH_{2n+2} , at least so far as it appears from analysis of distillates prepared on a laboratory scale, the lower distillates do contain members of the paraffine series.

The paraffine hydrocarbons with low boiling points, such as the butanes, pentanes, and hexanes, have an agreeable sweetish odor that is easily recognizable, and quite different from the pungent harsh odor of the methylenes. The odor of the paraffines is more apparent in the Miyagawa oil than in any other of the Japanese oils we have seen, and somewhat less in the Amaze oil. When these hydrocarbons with low boiling points are present, the crystalline paraffine hydrocarbons C_nH_{2n+2} are usually to be found.

Considerable quantities of gas were formerly obtained from the Amaze oil territory, but the supply now seems to be exhausted, at least so far as wells have been bored; some gas escapes from the shallow Miyagawa wells, more from the shallow wells of the Niitsu territory. As wells are sunk deeper in this territory it is probable that lighter oils will be found. On account of the friable condition of the oil rock and the danger of

clogging the wells by loose material, "shooting" the wells after boring is not practised. The flow from the wells is irregular; frequently it will amount to 300 barrels a day for a week, and then stop, and the oil must be pumped.

The oil territory in Japan includes the following fields:—Amaze, Nagaoka, Niitsu, and Hiyama. The different sections of the oil territory may be classified as follows:—

Amaze	$\left\{ \begin{array}{l} \text{Amaze} \\ \text{Miyagawa} \\ \text{Gendogi} \end{array} \right\}$	green oil
Nagaoka	$\left\{ \begin{array}{l} \text{Hirei} \\ \text{Kitatani} \\ \text{Katsudo} \end{array} \right\}$	dark oil
Niitsu	$\left\{ \begin{array}{l} \text{Koguchi} \\ \text{Kusodsu} \end{array} \right\}$	
Hiyama	$\left\{ \begin{array}{l} \text{Hiyama} \end{array} \right\}$	dark green oil

The Amaze field is the oldest; the Hiyama field has been most recently developed; both these oils contain paraffine.

The crude oils from the different fields differ essentially in their properties, as shown by the different specific gravity, the different percentages

	Amaze.	Hirei.	Katsudo.	Kitatani.	Koguchi.	Kusodsu.	Miyagawa.
Specific Gravity . . .	0.8245	0.8622	0.8771	0.8952	0.9435	0.9210	0.8911
Per cent Sulphur . . .	0.23	0.41	0.82	0.61	0.49	0.37	0.32
Per cent Nitrogen . . .	0.35	0.74	0.97	0.75	1.34	1.23	0.55
Iodine Absorption . . .	0.0	0.84	7.66	0.82	9.79	0.62	1.63
Coefficient of Expansion	82.5	78.5	76.5	79.5	67.5	61.5	74.5

PERCENTAGES OF DISTILLATES.

	Amaze.	Hirei.	Katsudo.	Kitatani.	Koguchi.	Kusodsu.	Miyagawa.
— 150°	22.8	21.8	22.2	14.	0.0	0.0	15.
150°—300°	40.2	38.3	38.8	38.8	25.0	25.0	36.8
+ 300°	37.	39.9	39.	47.2	75.	75.	48.2

of sulphur, nitrogen, and the different proportions in which they distil at different temperatures. There are also marked differences in iodine absorption, and in the coefficients of expansion. The latter were determined by ascertaining the specific gravity at 5° , 10° , 20° , and 25° , and dividing the differences in specific gravity at the different temperatures by five and multiplying the quotient by 100,000, the method described in Redwood's treatise on petroleum.

In the development of oil territory hitherto, no attempts have been made to ascertain the series of hydrocarbons which compose the main body of the crude oil. Beside the work of Pelouze and Cahours, Scholemmer, and Warren on the Pennsylvania and Canadian oils, and the work carried on in this Laboratory, no attempts have been made to determine the form of the hydrocarbons in the lower distillates of American oils, and nothing whatever beside the unpublished work of this Laboratory on the determination of the composition of the portions with higher boiling points. Beside the work of Markownikoff on the Russian oils and the work of Warren and Storer on Rangoon petroleum, very little has been done in this direction on oils from other fields. On account of the ease in the preparation of commercial products from the lighter oils of Pennsylvania and Ohio, the ultimate composition was of less importance than it is now becoming in the development of oil fields that yield heavier crude oils, such as the oil territory in California, Texas, South America, Japan, and numerous other fields recently discovered. The methods that must be applied to these heavy oils are essentially different from the methods that have been universally in use since the beginning of the oil industry. In Japan, the promoters of those oil fields will have the advantage not only of all former experience in oil refining, but the further advantage of a knowledge of the hydrocarbons which form the main body of the crude oils. Japanese petroleum apparently differs from other heavy petroleums in that it contains smaller amounts of the benzol homologues. Benzol and its homologues were found in the Amaze oil, and some of the other crude oils, but fuming sulphuric acid failed to reduce materially the specific gravity of several of the distillates that should yield benzol hydrocarbons, if they were present.

CONSTITUENTS OF PETROLEUM FROM THE AMAZE FIELD.

The lightest oil from the Japanese fields is found in the Amaze territory. It consequently contains the largest proportion of more volatile

constituents. A combustion of Amaze crude oil gave 84.66 per cent carbon and 13.22 per cent hydrogen. After several distillations under a Hempel column, fractions collected in larger quantities at 68°, 98°, 119°, 135°, 62°, 96°, 216°. No attempts were made to ascertain the form of the hydrocarbons below 68°. The distillate collected at 68° gave as its specific gravity 0.7343, which indicated that hexane was not present in any considerable quantity. But nothing further was done toward identifying hexamethylene, which no doubt is the principal hydrocarbon in this distillate.

The distillate collected at 98°-100°, after purifying with fuming sulphuric acid, gave as its specific gravity at 20°, 0.7450.

A combustion gave the following percentages of carbon and hydrogen:—

0.1347 grm. of the oil gave 0.4221 grm. CO₂ and 0.1721 grm. H₂O.

	Calculated for C ₆ H ₁₂ .	Found.
C	85.70	85.45
H	14.30	14.20

Its index of refraction was found to be 1.4174, and the molecular refraction, 33.14; calculated for C₇H₁₄, 32.22. This hydrocarbon was therefore methylhexamethylene.

The distillate 118°-120°, after purification with fuming sulphuric acid, gave 0.7621 as its specific gravity at 20°. A combustion gave the following percentages of carbon and hydrogen:—

0.1406 grm. of the oil gave 0.4378 grm. CO₂ and 0.1812 grm. H₂O.

	Calculated for C ₈ H ₁₆ .	Found.
C	84.70	84.94
H	14.30	14.33

A determination of the index of refraction of this oil gave 1.4256, and the molecular refraction, 37.68; calculated for C₈H₁₆, 36.82. This hydrocarbon was therefore dimethylhexamethylene.

The distillate collected at 134°-135° was purified with fuming sulphuric acid and analyzed.

0.1528 grm. of the oil gave 0.4805 grm. CO₂ and 0.1950 grm. H₂O.

	Calculated C ₉ H ₁₈ .	Found.
C	85.70	85.76
H	14.30	14.29

It gave as its specific gravity at 20°, 0.7787.

The refractive index of this oil was found to be 1.4348, and the molecular refraction, 42.27; calculated for C₉H₁₈, 41.42. This constituent was therefore trimethylhexamethylene.

A distillate collected in considerable quantity at 160°–162°, which was purified with fuming sulphuric acid and analyzed:—

0.2055 grm. of the oil gave 0.6445 grm. CO₂ and 0.2556 grm. H₂O.

	Calculated for C ₁₀ H ₂₀ .	Found.
C	85.70	85.50
H	14.30	13.82

This oil gave as its specific gravity at 20°, 0.7902. Its index of refraction was 1.4418, and its molecular refraction, 46.94; calculated for C₁₀H₂₀, 46.03.

The distillate at 190°–192°, after purification with fuming sulphuric acid, gave as its specific gravity at 20°, 0.8061. Its composition was determined by analysis:—

0.1612 grm. of the oil gave 0.5046 grm. CO₂ and 0.2025 grm. H₂O.

	Calculated for C ₁₁ H ₂₂ .	Found.
C	85.70	85.35
H	14.30	13.96

The molecular weight of this hydrocarbon at the freezing point of benzol was 156; calculated for C₁₁H₂₂, 154. The index of refraction at 20° was 1.4482, and the molecular refraction 51.24; calculated for C₁₁H₂₂, 50.63.

The distillate 212°–214°, purified with fuming sulphuric acid, gave as its specific gravity at 20°, 0.8165. A combustion gave the following proportions of carbon and hydrogen:—

0.1875 grm. of the oil gave 0.5879 grm. CO₂ and 0.2451 grm. H₂O.

	Calculated for C ₁₂ H ₂₄ .	Found.
C	85.70	85.51
H	14.30	14.52

A determination of its molecular weight at the freezing point gave 172; calculated for C₁₂H₂₄, 168. Its index of refraction was 1.4535, and the molecular refraction, 55.76; calculated for C₁₂H₂₄, 55.23.

COMPOSITION OF THE PORTIONS OF JAPANESE PETROLEUM WITH HIGH BOILING POINTS.

Japanese petroleum from different sources differs materially in its composition. From such oils as the Hirei no crystalline solids can be separated, even at low temperatures. But from others, such as the Amaze, Miyagawa, and Hiyama, crystalline solids separate from the higher fractions. The fraction 310°—315° atmospheric pressure, from Amaze crude oil became solid on cooling. The solid portion was separated by cooling and filtration; it was washed, pressed, and warmed with gasoline which removed all color. Melting point, 68°. The fractions above 225° were collected *in vacuo* under 30 mm. The purified solid from 225°—230° melted at 70°, that from 250°—275° at 73°, and that from 260°—265° at 74°. The solid from 225°—230° gave, by combustion, values showing it to belong to the series C_nH_{2n+2} .

0.1535 grm. of the oil gave 0.4890 grm. CO_2 and 0.1787 grm. H_2O .

	Calculated for $C_{12}H_{24}$	Calculated for C_nH_{2n}	Found.
C	85.14	85.70	85.29
H	14.86	14.30	14.99

The fraction 250°—260°, 30 mm., from the Amaze oil gave the following percentages by combustion, also showing the series C_nH_{2n+2} :—

0.1654 grm. of the oil gave 0.5161 grm. CO_2 and 0.2233 grm. H_2O .

C	85.03
H	15.00

A combustion of the fraction 265°—270° gave values required for a hydrocarbon of the series C_nH_{2n+2} :—

0.1750 grm. of the oil gave 0.5469 grm. CO_2 and 0.2346 grm. H_2O .

C	85.21
H	14.81

In determining the molecular weight of this hydrocarbon at the boiling point of benzol, the following result was obtained:—

0.4190 grm. of the oil and 24.3 grms. benzol gave a rise in boiling point of 0.126.

Calculated for $C_{26}H_{54}$	Found.
367	367

Determinations by the boiling point method of hydrocarbons with such high molecular weights are of necessity somewhat uncertain on account of the slight rise in boiling point. The question of the molecular weights of these solid hydrocarbons will receive more attention with the constituents of Pennsylvania and California petroleums with high boiling points.

The specific gravity of the solid 250° - 260° is nearly the same as that of the corresponding hydrocarbon from Pennsylvania petroleum:—

	Japanese, 250° - 260° , 30 mm.	Pennsylvania,* 292° - 295° , 50 mm.
60		0.7977
70	0.7943	0.7950
80	0.7920	0.7943
90	0.7918	

The specific gravity of the Japanese solid at 60° could not be determined, because it was not liquid at that temperature.

MIYAGAWA PETROLEUM.

Although this oil is from a field situated only six miles from the Amaze field, it differs essentially in its specific gravity, and in the proportions in which it distils, from the Amaze oil. The crude oil was distilled under atmospheric pressure, and the distillation of the lower portions continued until they came together in larger quantities at temperatures at which distillates were collected from the other oils. The specific gravity of the distillates after treating with concentrated sulphuric acid is as follows:—

98° - 100° .	118° - 120° .	134° - 136° .	160° - 162° .	194° - 196° .	212° - 214° .	228° - 230° .
0.7364	0.7631	0.7772	0.8088	0.8493	0.8674	0.8770

The last three fractions were also treated with fuming sulphuric acid and the specific gravity determined:—

194° - 196° .	212° - 214° .	228° - 230° .
0.8412	0.8650	0.8720

The slight change after the thorough treatment with fuming sulphuric acid shows that no benzol homologues were present in these portions, yet the specific gravity of the hydrocarbons above 196° is considerably higher than of those from Amaze oil or from Hirei oil. The distillates

* Unpublished data.

collected under atmospheric pressure were thoroughly treated with fuming sulphuric acid, washed, dried, and their molecular refraction determined : —

Distillate.	Refractive Index.	Molecular Refraction.	
		Calculated.	Required.
98°-100°	1.4117	33.14	32.21
118°-120°	1.4163	36.92	36.82
134°-136°	1.4261	41.51	41.42
160°-162°	1.4463	46.26	46.03
194°-196°	1.4605	50.27	50.63
214°-216°	1.4706	54.34	55.23

HIREI PETROLEUM.

A combustion of Hirei crude oil gave 82.28 per cent of carbon and 13.19 per cent of hydrogen. In the distillation of the Hirei oil, fractions collected within the same limits of temperature as those from the other crude oils. The distillate collecting in the vicinity of 98°, after treatment with sulphuric acid, gave 0.7412 as its specific gravity. Its molecular weight at the freezing point of benzol was 98; required for C_7H_{14} , 98. Its index of refraction was 1.4095, and its molecular refraction, 32.77; required for C_7H_{14} , 32.22.

The fraction 118°-120° gave as its specific gravity 0.7523. Its molecular weight was 114; required for C_8H_{16} , 112. Its index of refraction was 1.4151, and its molecular refraction, 37.34; required for C_8H_{16} , 36.82.

The fraction at 135° gave as its specific gravity 0.7676. Its molecular weight was 128; required for C_9H_{18} , 126. Its index of refraction was 1.4372, and its molecular refraction, 42.12; required for C_9H_{18} , 41.42.

The fraction 162° gave for its specific gravity 0.7887. Its molecular weight was found to be 137; required for $C_{10}H_{20}$, 140. Its index of refraction was 1.4372, and its molecular refraction, 46.60; required for $C_{10}H_{20}$, 46.03.

The specific gravity of the fraction at 196° was 0.8192. Its index of

refraction was 1.4516, and its molecular refraction, 50.78; required for $C_{11}H_{22}$, 50.63.

The specific gravity of the fraction 216° was 0.8327, and the molecular weight, 172; required for $C_{12}H_{24}$, 168. Its index of refraction was 1.4599, and its molecular refraction, 55.22; required for $C_{12}H_{24}$, 55.23.

The specific gravity of these distillates from Hirei oil is somewhat higher than was found in the corresponding distillates from Amaze oil, and the differences increase with increasing molecular weights. It was at first thought that this was due to incomplete removal of benzol hydrocarbons, but still further treatment with fuming sulphuric acid failed to diminish these values. It is probable that the oil contains hydrocarbons with more than one methylene ring.

The results of this examination show that Japanese petroleum is composed for the greater part of hydrocarbons of the series C_nH_{2n} , — the methylene hydrocarbons. Probably the very heavy oils contain hydrocarbons with two or more methylene rings, of the series C_nH_{2n-2} or C_nH_{2n-4} . Some of the oils contain solid paraffine hydrocarbons, others do not. The proportion of benzol derivatives in the oils examined is relatively much smaller than in California petroleum. The proportion of nitrogen compounds and of sulphur compounds is quite variable. In some of the oils the percentages were nearly as large as any found in California petroleum, in others the amounts were much smaller.